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(54) **Aqueous fertiliser solutions**

(57) The present invention provides a fertiliser composition in the form of an aqueous solution of urea, ammonium nitrate, ammonia or a mixture thereof and dicyandiamide in an amount such that the dicyandiamide nitrogen is 10% or more by weight of the total nitrogen of said solution.

The present invention also provides a fertiliser composition consisting essentially of an aqueous solution of urea, ammonium nitrate, ammonium sulphate, ammonia or a mixture thereof, said solution having micronutrients dissolved therein and containing a stabilising amount of dicyandiamide to maintain the micronutrients in solution.

Furthermore, the present invention provides a method of making a fertiliser solution, which comprises preparing an aqueous solution of urea, ammonium nitrate, ammonia or a mixture thereof and dissolving crystalline dicyandiamide therein.

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SPECIFICATION

**Aqueous fertiliser solutions**

The present invention is concerned with fertiliser solutions based on nitrogen compounds, which solutions may also contain phosphates and/or potassium salts, as well as micronutrients.

The use of fertilisers in liquid form is known. The increasing interest in this form of fertiliser is due, in particular, to the fact that liquid fertilisers can be offered at a low price, they are easy to handle, they make possible exact dosing, different fertilisers can be readily mixed with each other and plant protection agents can be applied, together with the fertiliser solution, in a single operation.

The application of large amounts of nitrogen per unit area in one operation, while it saves operating expenses, has the disadvantage that losses of nitrogen can occur by washing out and denitrification and, since the nutrient substances are not applied continuously but at a single time, the plants are stimulated by the sudden addition of nutrient substance to sustain a sudden and unhealthy growth.

With nitrogen fertilisers in solid form, these disadvantages are avoided by providing the fertiliser granules with waxes, resins or other coatings in order to obtain a regulated, continuous liberation of the fertiliser nutrients. It is also known to add nitrification inhibitors, i.e. compounds which retard the rapid conversion of ammonium nitrogen into nitrate nitrogen by the bacteria of the soil.

When high doses of nitrogen per unit area in the form of fertiliser solutions are applied in a single operation, the above-mentioned disadvantages can be reduced by admixing nitrification-inhibiting substances to the solution. The known nitrification inhibitor, 2-chloro-6-trichloromethylpyridine, due to its volatility, requires immediate incorporation of the mixtures into the soil, i.e., an additional amount of work.

Dicyandiamide also has a nitrification-inhibiting action. It is a solid, crystalline, physiologically unobjectionable substance of high melting point and is produced industrially in large quantities from calcium cyanamide.

French Patent Specification No. 1,232,366 proposes the addition of dicyandiamide as nitrification inhibitor in amounts of up to 30% to solid ammonium or urea fertilisers. The addition of dicyandiamide to nitrogen-containing fertilisers is also recommended in German Patent Specification No. 2,051,935.

Upon further study of the use of dicyandiamide as a nitrification inhibitor, we have found that sufficient retardation of the nitrification occurs when at least 10% by weight of dicyandiamide nitrogen is present, based on the total nitrogen of a fertiliser. To the best of our knowledge, it has hitherto not been possible to consider the use of dicyandiamide in fertiliser solutions since this compound dissolves in water only to an extent of 1.27% by weight at 0°C. and of 3.33% by weight at 20°C. As is known, the solubility of dicyandiamide in most salt solutions is even less than this, so that a combination of dicyandiamide with aqueous fertiliser solutions has hitherto not even been attempted. It has, therefore, been a problem to find a fertiliser solution into which dicyandiamide can be introduced in sufficient amount for it to manifest its activity as a nitrification inhibitor.

Another problem which has been encountered in the manufacture of liquid fertilisers relates to the inclusion of micronutrients therein. The increasing use of liquid fertilisers makes necessary for special uses and particularly for intensive methods of cultivation, not only a sufficient supply of the principal plant nutrients, namely, nitrogen, phosphorus and potash, but also a certain amount of micronutrients, i.e., trace elements usually in the form of inorganic salts and particularly metal salts. However, the production of such nutrient solutions gives rise to certain difficulties since most metal salts are sparingly soluble in ordinary nutrient solutions. Furthermore, chemical reactions between the individual compounds cannot always be avoided and may lead to the formation of the undesired precipitates. Consequently, these previously known solutions must be applied immediately after the addition of the micro-nutrients thereto.

It is known that the solubility of many trace elements can be increased by the addition of chelating agents, amino acids primarily being used for this purpose. It has been found that, by using amino acids, the effectiveness of the trace elements is substantially increased and that only 1/5 to 1/10 of the amount otherwise necessary is required. However, such chelating agents are relatively expensive.

It is, therefore, an object of the present invention to provide an aqueous fertiliser solution having improved nitrification-inhibiting properties. It is another object of the present invention to provide an aqueous fertiliser solution which has an increased solubility for micronutrients and which increases the stability of micronutrients dissolved therein.

Thus, according to the present invention, there is provided a fertiliser composition in the form of an aqueous solution of urea, ammonium nitrate, ammonia or a mixture thereof and dicyandiamide in an amount such that the dicyandiamide nitrogen is 10% or more by weight of the total nitrogen of said solution.

In general, the present invention is based on the discovery that both of these objectives can be attained by utilising certain aqueous fertiliser solutions having dicyandiamide dissolved therein. Considering first the problem of attaining improved nitrification inhibition, the solution of this problem disclosed herein is based on our discovery that aqueous solutions of certain nitrogen-containing compounds commonly used in commercial fertilisers are capable of dissolving substantially greater

quantities of dicyandiamide than can be dissolved in pure water. More particularly, we were suprised to find that aqueous solutions of a nitrogen-containing compound selected from urea, ammonium nitrate, ammonia and mixtures thereof are capable of dissolving quantities of dicyandiamide well above the amounts required to achieve a nitrification-inhibiting effect, i.e., above the concentrations at which the dicyandiamide nitrogen is 10% or more of the total nitrogen in the solution.

It may be noted that not all nitrogen-containing compounds have the property of increasing the solubility of dicyandiamide in aqueous solutions of such compounds. Thus, as indicated in the data given in the following Examples, ammonium sulphate alone or in combination with ammonium phosphate fails to produce the desired increase in the solubility of dicyandiamide. On the other hand, the addition of ammonium sulphate to an aqueous solution containing ammonium nitrate, urea or ammonia does not appear to have a detrimental effect on the solubilising properties of such a solution.

We have also found that other common fertiliser compounds, such as phosphates and soluble potassium salts, can be added to solutions of such nitrogen compounds without impairing their ability to dissolve relatively large amounts of dicyandiamide. Hence, in accordance with the present invention, it is possible to formulate multi-nutrient fertiliser solutions containing, in addition to the dicyandiamide-solubilising compounds referred to above, other fertiliser compounds, such as commercial diammonium phosphate and potassium chloride, as well as ammonium sulphate, if desired.

In addition, we have found that aqueous fertiliser compositions of the type described above are capable of dissolving significantly increased amounts of micro-nutrients. It may be noted that where the aqueous fertiliser solution containing dicyandiamide is prepared primarily to achieve an increase in micronutrient content, the amount of dissolved dicyandiamide is less critical than where inhibition of nitrification is desired. Thus, whereas a solution containing at least about 10% of dicyandiamide nitrogen is required to achieve acceptable inhibition of nitrification, increases in micronutrient solubility can be achieved with relatively small amounts of dissolved dicyandiamide.

Consequently, the present invention also provides a fertiliser composition consisting essentially of an aqueous solution of urea, ammonium nitrate, ammonium sulphate, ammonia or a mixture thereof, said solution having micronutrients dissolved therein and containing a stabilising amount of dicyandiamide to maintain the micronutrients in solution.

Furthermore, a wider variety of nitrogen-containing fertilisers can be used in solutions wherein the dicyandiamide is used to enhance solubility of micronutrients. For example, whereas, as indicated below, aqueous fertiliser solutions containing ammonium sulphate as the sole fertiliser component are incapable of dissolving at 20°C. an amount of dicyandiamide corresponding to 10% by weight of dicyandiamide nitrogen, ammonium sulphate-containing solutions can be used to obtain liquid fertilisers of relatively high micronutrient content since relatively small amounts of dicyandiamide are capable of increasing the micronutrient solubility of the solution. More generally, the nitrogen-containing compound used in such solutions may be any of the commonly used fertilisers, such as urea, ammonium nitrate, ammonium sulphate or ammonia, in liquified form or as a concentrated aqueous solution. Such solutions may also contain mixtures of these nitrogen compounds and phosphates and/or potassium salts may also be added without the solubility of the dicyandiamide, and thus of the micronutrients, thereby being reduced.

The preferred quantity of dicyandiamide for either nitrification inhibition or micronutrient solubilisation and stabilisation is that amount required to provide at least about 10% dicyandiamide nitrogen based on the total amount of nitrogen in the solution. Using such solutions, a micronutrient concentration of, for example, 0.1% to 1.5% can be achieved. The upper limit on the amount of the dicyandiamide does not appear to be critical and may be the maximum amount that can be dissolved in the fertiliser solution, for example, about 35%. Dicyandiamide considerably increases the solubility of many trace nutrients in fertiliser solutions and stabilises such solutions for a long time. Furthermore, it makes it possible to prepare fertiliser solutions containing micronutrients at the fertiliser manufacturing plant in the form of a concentrate, for example in unit packages.

As micronutrients, there are used, in particular, the following elements, in the form of their water-soluble salts: boron, iron, cobalt, copper, manganese, molybdenum, nickel and zinc. The addition of other trace elements is also possible.

We were surprised to find that the stability of the nutrient solutions containing the metal salts is retained for a long time in the presence of dicyandiamide. The solutions remain clear and do not form precipitates, even at low temperatures.

The examples given hereinafter show that, in the fertiliser solutions containing dicyandiamide, as much as several times the amount of trace elements can be introduced as can be dissolved in solutions containing no dicyandiamide. Furthermore, dicyandiamide prevents the formation of hydroxide and oxide precipitates in the case of elements which are easily hydrolysable and oxidisable, this being particularly noteworthy in the case of ferrous and manganese salts. Without dicyandiamide, deposits of insoluble ferric hydroxide and manganese dioxide precipitate from the solutions after only a short time. However, in the presence of dicyandiamide, these solutions remain clear, even when stored for long periods of time.

We have also found that, as a result of the presence of dicyandiamide, the strongly corrosive effect of ordinary fertiliser salt solutions, particularly with respect to iron, is considerably reduced.

Any dicyandiamide of technically pure grade can be used according to the present invention. The more finely granular is the dicyandiamide used, the greater is its rate of dissolution. The establishment of a concentration of 10% by weight of dicyandiamide nitrogen based on the total nitrogen content of the solution takes place rapidly and without problems at a temperature of about 20°C. Even upon cooling the solutions to below ambient temperature, no precipitation of dicyandiamide crystals takes place at a concentration of 10% by weight of dicyandiamide nitrogen. Even at 0°C., no dicyandiamide crystallises out upon storage from solutions of nitrogen-containing compounds containing 10% by weight of dicyandiamide nitrogen. In the case of phosphate- and potassium-containing solutions which also contain nitrogen compounds, which solutions cannot be prepared in such high concentrations as solutions having only nitrogen-containing compounds, we found it surprising that although dicyandiamide is the most sparingly soluble of the fertiliser components in the solution, potassium nitrate, for example, crystallises out before the dicyandiamide.

We were also surprised to find that the stability of the dicyandiamide introduced into the different fertiliser solutions remains unchanged. Even upon storage of the solutions for several weeks at about 20°C., no change in the dicyandiamide concentration was observed and no formation of dicyandiamide-urea or other possible reaction products was observed.

The fertiliser solutions according to the present invention containing dicyandiamide can be produced in a simple manner by adding the calculated quantity of solid dicyandiamide to the solutions containing the nitrogen compounds and mixing for a short time.

The following Examples are given for the purpose of illustrating the present invention:—

EXAMPLE 1

TABLE 1

Composition of the fertiliser solution in % by weight

| ammonium nitrate | urea | water | $NH_3$ | ammonium sulphate | ammonium phosphate | g. of dicyandiamide dissolved in 100 g. fertiliser solution | % by weight of dicyandiamide N referred to total N of the fertiliser solution |
|---|---|---|---|---|---|---|---|
| 39.5 | 30.5 | 30 | — | — | — | 6.8 | 16.2 |
| 69.1 | 7.7 | 23.2 | — | — | — | 6.0 | 14.4 |
| — | 16.0 | 50 | — | 34 | — | 6.0 | 26.6 |
| 14.5 | 11.5 | 50 | — | 24 | — | 7.7 | 32.4 |
| — | 37.5 | 58.2 | 4.3 | — | — | 7.2 | 22.8 |
| 33.3 | 6.1 | 45.5 | 15.1 | — | — | 13.3 | 32.6 |
| *— | — | 57 | — | 22 | 21 | 1.1 | 7.8 |

*Comparative Example.

Table 1 clearly shows the high solubility of dicyandiamide in fertiliser solutions containing nitrogen compounds, such as urea and ammonium nitrate, and also shows that this effect is not obtained with ammonium sulphate. The difference in solubility of dicyandiamide as a function of the nitrogen compounds in the solution can also be seen from the Table.

EXAMPLE 2

This Example illustrates the variations in the solubility of dicyandiamide at 20°C. in fertiliser solutions containing nitrogen compounds and phosphate.

In an aqueous solution containing a nitrogen compound and phosphate in equal portions of nitrogen and phosphorus pentoxide, ammonium sulphate is replaced by:

a) ammonium nitrate + urea
b) ammonium nitrate
c) urea

the total nitrogen content being kept the same. The resulting dicyandiamide solutions are shown in the following Table 2.

As is shown by the formulations, it is possible, by replacing ammonium sulphate by ammonium nitrate or urea or a mixture thereof, to increase the percentage of dissolved dicyandiamide to such an extent that, at 20°C., the dicyandiamide nitrogen content of dicyandiamide-saturated solutions is far above 10% of the total nitrogen.

TABLE 2

Composition of the solution in % by weight

| | ammonium sulphate | ammonium nitrate | urea | * diammonium hydrogen phosphate $(NH_4)_{1.7}H_{1.3}PO_4$ | solubility of dicyandiamide in g/100 g of solution | % by weight of dicyandiamide N referred to total nitrogen |
|---|---|---|---|---|---|---|
| comparison | 31.2 | — | — | 13.9 | 1.1 | 6.9 |
| a | — | 9.9 | 7.4 | 18.9 | 3.8 | 13.0 |
| b | — | 19.8 | — | 18.9 | 3.6 | 22.8 |
| c | — | — | 14.8 | 18.9 | 4.4 | 28.0 |

*In order to prepare solutions containing a higher concentration of nitrogen and phosphorus, a mixture of mono- and diammonium phosphates is used in the ratio indicated. This mixture has a greater solubility in water than that of the pure salts.

EXAMPLE 3

Solubility of dicyandiamide in fertiliser solutions.

a) Dicyandiamide is introduced to saturation level at 20°C. into an aqueous solution containing nitrogen, phosphorus and potassium compounds and consisting of:

8.1% by weight ammonium nitrate
9.7% by weight urea
4.1% by weight potassium chloride
16.7% by weight $(NH_4)_{1.7}H_{1.3}PO_4$
61.4% by weight water.

The dicyandiamide dissolves in an amount of up to 4.6% by weight. Based on the total nitrogen content of the fertiliser solution, this is equal to 29% by weight of nitrogen in the form of dicyandiamide.

In another portion of this solution containing nitrogen, phosphorus and potassium compounds, 1.58% by weight of dicyandiamide (= 10% by weight of dicyandiamide nitrogen based on the total nitrogen) is dissolved. The solution is slowly cooled until crystallisation occurs, the first crystals depositing at 0°C. Upon examination of these crystals, it is found that they consist of precipitated potassium nitrate (formed from the reaction $KCl + NH_4NO_3 \rightarrow KNO_3 + NH_4Cl$) and not dycandiamide.

b) 4.2% by weight of dicyandiamide (= 10% by weight of dicyandiamide nitrogen based on the total nitrogen) is dissolved in a nitrogen fertiliser solution consisting of:

39.5% by weight ammonium nitrate
30.5% by weight urea
30% by weight water

in which up to 6.8% by weight of dicyandiamide is capable of being dissolved at 20°C. The solution is slowly cooled to —10°C. No crystals precipitate.

c) 2.5% by weight dicyandiamide (= 10% by weight dicyandiamide nitrogen referred to total nitrogen) is dissolved in a nitrogen fertiliser solution consisting of:

24% by weight ammonium sulphate
14.5% by weight ammonium nitrate
11.5% by weight urea

The solution remains clear upon cooling to —5°C.

EXAMPLE 4

This example illustrates the effect of dicyandiamide on the solubility of various trace nutrients in fertiliser solutions containing nitrogen compounds.

Various trace elements were dissolved up to saturation level at 20°C. in each of two fertiliser

solutions (A) and (B). Solution A contained, by weight, 24% ammonium sulphate, 14.5% ammonium nitrate, 11.5% urea and 50% water. Solution B had the same composition as solution A except that it also contained 2.4% by weight of dicyandiamide, which corresponds to 10% by weight of dicyandiamide nitrogen based on the total nitrogen in the solution. The results of these solubility tests are summarised in the following Table 3:

TABLE 3

| Component | Solution A | Solution B |
|---|---|---|
| borax decahydrate | 6% | 8% |
| cupric sulphate pentahydrate | 0.3% | 4% |
| ammonium molybdate tetrahydrate | 1% | 2% |
| zinc sulphate heptahydrate | 0.18% | 0.5% |
| cobalt nitrate hexahydrate | 1% | 4.8% |
| nickel nitrate hexahydrate | 0.32% | 1.15% |

It can be seen from the above data that dicyandiamide is capable of substantially increasing the solubility of the micronutrient salts.

EXAMPLE 5

This Example illustrates the improved stability of trace nutrients in fertiliser solutions containing dicyandiamide.

a) 0.1% by weight of ferric sulphate pentahydrate is dissolved in each of the fertiliser solutions A and B as in Example 4. After storage for one week, the dicyandiamide-containing solution is still completely clear, whereas the solution without dicyandiamide shows deposits of ferric hydroxide.

b) 0.5% by weight of manganese sulphate monohydrate is dissolved in each of solutions A and B of Example 4. After storate for four weeks, the dicyandiamide-containing solution is still completely clear, whereas the solution without dicyandiamide shows a precipitate of dark-brown manganese dioxide after only a few days.

EXAMPLE 6

This Example illustrates the stability of a fertiliser solution based on commercial nitrogen fertilisers and containing dicyandiamide and numerous trace elements.

4.2% by weight of dicyandiamide, which is equivalent to 10% by weight dicyandiamide nitrogen based on total nitrogen, is dissolved in a fertiliser solution consisting of:

39.5% by weight ammonium nitrate
30.5% by weight urea
30.0% by weight water

and 0.1% by weight of each of the following trace elements is dissolved therein:

boric acid
manganese chloride tetrahydrate
ammonium molybdate tetrahydrate
cobalt nitrate hexahydrate
nickel nitrate hexahydrate
cupric nitrate pentahydrate
zinc chloride.

The resultant solution remains clear for several weeks, without forming a deposit.

EXAMPLE 7

This Example illustrates a stable nitrogen fertiliser solution containing a potassium compound, dicyandiamide and trace elements.

2.25% by weight of dicyandiamide, equivalent to 10% by weight of dicyandiamide nitrogen based on total nitrogen, is dissolved in a fertiliser solution consisting of:

32% by weight urea
15.8% by weight potassium chloride
48.2% by weight water

0.1% by weight of each of the following micronutrients is added thereto:

boric acid
manganese chloride tetrahydrate
ammonium molybdate tetrahydrate
cobalt nitrate hexahydrate
nickel nitrate hexahydrate
cupric sulphate pentahydrate
zinc chloride

A clear solution is obtained which remains stable for several weeks.

In another solution of the same composition, the following micronutrients are dissolved in a quantity of 0.1% by weight each:

boric acid
manganese chloride tetrahydrate
magnesium chloride hexahydrate
zinc sulphate heptahydrate
ammonium molybdate tetrahydrate

A clear solution is again obtained which remains stable for several weeks.

EXAMPLE 8

This Example illustrates a stable nitrogen/phosphorus/potash (NPK) fertiliser solution which additionally contains micronutrients.

1.58% by weight of dicyandiamide, equivalent to 10% by weight of dicyandiamide nitrogen based on total nitrogen, is dissolved in an aqueous fertiliser solution consisting of the following compounds containing nitrogen, phosphorus and potassium:

8.1% by weight ammonium nitrate
9.7% by weight urea
4.1% by weight potassium chloride
16.7% by weight diammonium hydrogen phosphate $(NH_4)_{1.7}H_{1.3}PO_4$)
64.4% by weight water

The following quantities of micronutrients are added thereto:

0.5% by weight borax
0.1% by weight ammonium molybdate
0.1% by weight potassium chromate
0.1% by weight potassium bromide
0.1% by weight potassium iodide

A stable, clear fertiliser solution is obtained.

CLAIMS

1. A fertiliser composition in the form of an aqueous solution of urea, ammonium nitrate, ammonia or a mixture thereof and dicyandiamide in an amount such that the dicyandiamide nitrogen is 10% or more by weight of the total nitrogen of said solution.

2. A composition according to claim 1, wherein the aqueous solution additionally contains dissolved therein ammonium sulphate and/or at least one water-soluble phosphate and/or at least one water-soluble potassium salt.

3. A fertiliser composition consisting essentially of an aqueous solution of urea, ammonium nitrate, ammonium sulphate, ammonia or a mixture there, said solution having micronutrients dissolved therein and containing a stabilising amount of dicyandiamide to maintaint the micronutrients in solution.

4. A fertiliser composition according to claim 3, wherein the solution contains a phosphorus-containing fertiliser compound dissolved therein.

5. A fertiliser composition according to claim 3 or 4, wherein the solution contains a potassium-containing fertiliser compound dissolved therein.

6. A fertiliser composition according to any of claims 3 to 5, wherein the dicyandiamide nitrogen in the solution is at least about 10% by weight of the total nitrogen in said solution.

7. A fertiliser composition according to claim 6, wherein the dicyandiamide nitrogen in the solution is from about 10% to about 35% by weight of the total nitrogen in the solution.

8. A fertiliser composition according to any of claims 3 to 7, wherein the micronutrients are metal salts.

9. A fertiliser composition according to any of claims 3 to 8, wherein the micronutrients comprise from about 0.1 to about 1.5% by weight of the solution.

10. Fertiliser compositions according to any of claims 1 to 9, substantially as hereinbefore described and exemplified.

11. A method of making a fertiliser solution, which comprises preparing an aqueous solution of urea, ammonium nitrate, ammonia or a mixture there and dissolving crystalline dicyandiamide therein.

12. A method according to claim 11, wherein there is additionally dissolved in the aqueous

solution at least one micronutrient and/or ammonium sulphate and/or a phosphorus-containing fertiliser compound and/or a potassium/containing fertiliser compound.

13. A method according to claim 11 or 12 of making a fertiliser solution, substantially as hereinbefore described and exemplified.

14. A fertiliser solution, whenever made by the method according to any of claims 11 to 13.

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